THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF

THE MINERALOGICAL SOCIETY

No. 216 March, 1952 Vol. XXIX

The graphitization of diamond and the nature of cliftonite.

(With Plate XXVI.)

By H. J. Grenville-Wells, M.Sc., Ph.D.

University College, London.

[Read January 24, 1952.]

1. *Introduction.*

It has long been known that if a diamond is heated in pure oxygen, or even in air, to a temperature of about 700° C. or higher (depending on the initial quality of the diamond), it will be wholly or partially oxidized to CO or CO_2, but that if the diamond is heated in the absence of oxygen—preferably in vacuo—to a temperature of about 1500° C. or higher (again depending on the initial quality of the diamond), it will be wholly or partially converted to graphite. For complete conversion the graphite is always polycrystalline. The *partial* conversion of diamond to graphite is, however, of considerable interest, because when graphite forms on a single crystal of diamond it exhibits a strong preferred orientation. It was hoped by the study of such graphitized diamonds to obtain information on the following four questions:

(*a*) *The origin of cliftonite.*—The detailed investigation of this preferred orientation was undertaken mainly because of an interest in the formation of the mineral cliftonite. This is a graphite of *cubic* habit which is found in some meteorites, and it has been studied by several investigators, mainly, however, before the development of X-ray crystallography—references to this early work can be found, for example, in a book by A. E. Fersman and V. Goldschmidt.[1] It has been conjectured

[1] A. von Fersmann [A. E. Fersman] and V. Goldschmidt, Der Diamant. Heidelberg, 1911. [Min. Mag. **16**–164.]

that cliftonite is a pseudomorph after diamond, but a single X-ray photograph published by M. H. Hey[1] made this appear very unlikely, and it was therefore decided to make direct comparative experiments to test the hypothesis, the necessary detailed examination of cliftonite being made at the same time.

(*b*) *The origin of the graphite on graphite-coated diamonds.*—Diamonds coated with a thin layer of graphite are found in the Premier diamond mine, South Africa,[2] and might have originated (i) by direct crystallization of additional carbon on the diamond crystal after the conditions favouring the formation of diamond had altered, or (ii) from the conversion of the surface layers of the diamond to graphite due to a subsequent increase in temperature, or other appropriate change. Hence, if the orientation of the graphite could be determined on both naturally and artificially graphitized diamonds, this point might be cleared up.

(*c*) *The nature of the graphite produced when diamond is graphitized.*—There are two recognized forms of graphite;[3] in the common form successive hexagonal layers of carbon atoms can be thought of as being related to each other by hexagonal close-packing (2-layer structure), while in the rare form successive layers are related as in cubic close-packing (3-layer structure, space-group $R\bar{3}m$). The rare form seems to be present to the extent of about 4–14 % in different natural and artificial graphites, and the percentage can sometimes be increased by mechanical working[4] or decreased by chemical action (Lipson and Stokes, loc. cit.).

Now, if a diamond is thought of as consisting of a series of hexagonal 'aliphatic' layers normal to the trigonal axis, the structure will be analogous to that of the rare form of graphite, in which the layers are 'aromatic' but arranged in the same way. Thus, if a diamond is converted to graphite, it is possible that such graphite would be mostly, if not exclusively, of the rare form. This was indeed suggested by Nath,[5] but he did not quote experimental evidence in support of his view that this was the transition structure between graphite and diamond, and direct evidence is still required.

(*d*) *The possibility of altering diamond by heat-treatment.*—Diamond is

[1] M. H. Hey, Min. Mag., 1938, vol. 25, p. 81.

[2] P. A. Wagner, Trans. Geol. Soc. South Africa, 1915, vol. 17 (for 1914), p. 29.

[3] H. Lipson and A. R. Stokes, Proc. Roy. Soc. London, Ser. A, 1942, vol. 181, p. 101. [M.A. **8**–284.]

[4] G. Bacon, Acta Cryst., 1950, vol. 3, p. 137. [M.A. **11**–235.]

[5] N. S. N. Nath, Proc. Indian Acad. Sci., Sect. A, 1935, vol. 1, p. 841. [M.A. **6**–200.]

extremely resistant to chemical attack, and cannot be plastically deformed, at least not under laboratory conditions, and from the experimental point of view it would be very useful if diamond could be altered in a reproducible way; in particular if Type I could be changed into Type II, and vice versa. Heat-treatment suggests itself as a possible method of effecting such alterations, and partially graphitized diamonds will almost certainly be a by-product of any such experiments.

2. *Experimental material.*

In order to gain a general idea of the type of results to be expected, X-ray photographs were taken of a number of diamonds which had been subjected to various kinds of heat-treatment (kindly lent to me by Mr. P. Grodzinski), although the nature of diamonds before treatment was, from an X-ray standpoint, unknown.

Attempts were also made to graphitize diamonds in a carbon arc, and several diamonds were successfully graphitized in a vacuum furnace.

Graphite-coated diamonds from Premier mine, and samples of Fletcher's original batch of cliftonite were made available by the British Museum.

3. *Experimental results and discussion.*

(*a*) *The preferred orientation of the graphite.*—In this work only the (0002) graphite ring obtained with Cu-$K\alpha$ radiation has been studied, i.e. information has been sought on the orientation of the *hexagonal* axis of the graphite relative to the main crystal. The chart in fig. 1 shows the appearance on a stereographic projection of a small circle of radius $[90° - \theta_{(0002)}]$—originally parallel to the plane of projection—rotated through successive intervals of 5° about the 90–90° vertical line of the diagram. It is a useful time-saving device when plotting the pole-figures from the X-ray photographs. A pole-figure frequently shows some symmetry, and then only a limited section of the sphere need be investigated. In both cases considered here the symmetry is *m*3*m*, and thus if the crystal is mounted with [001] vertical and rotated over a range of 45°, starting with the X-rays along [100], the whole pattern can be obtained.

(i) *Graphitized diamond.*—The preferred orientation of the graphite formed on a *cube* and on an *octahedron* was *geometrically identical*, allowance being made for the larger quantity of graphite present on the cube. Representative Laue photographs are shown in fig. 2. Further, the orientation was relatively sharp, as can be seen from the pole figure in

fig. 3A. It seems, therefore, that the formation of graphite on diamond, at least in vacuo, is, as had been anticipated, *characterized by the association of the hexagonal axis of the graphite with the trigonal axis of the diamond; and is independent of the habit of the diamond.*

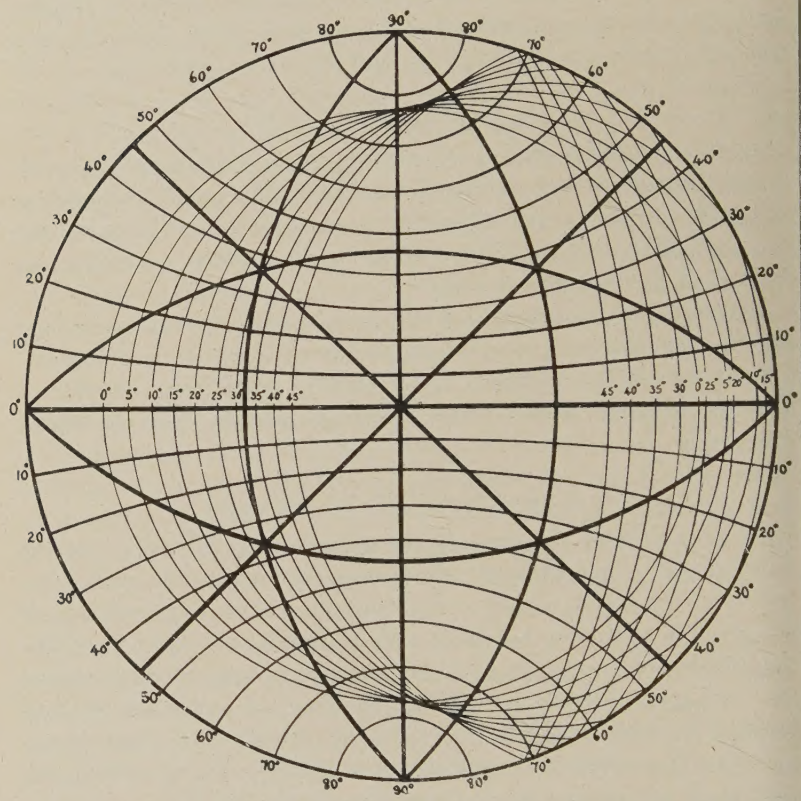


FIG. 1. Chart for the determination of the preferred orientation of graphite found for cliftonite and heat-treated diamonds. [Cu-$K\alpha$ and (0002): i.e. $\theta = 13{\cdot}2°$.] The cubic symmetry of the substrate results in the preferred orientation diagram having planes of symmetry as shown by the heavy lines, and thus rotation about [001] over a range of 45°, starting with the X-ray beam along [100], is sufficient for the determination of the complete pattern.

This independence was not necessarily to be expected; since graphite is a tabular crystal, it was quite possible that it would simply form plates on whatever surface of diamond was available, and hence the association of the [0001] axis with the trigonal axis of an octahedron would have been expected anyway. The naturally occurring graphite-coated dia-

monds are reported to show flakes or plates of graphite on their surfaces, which could be in accordance with this hypothesis. In this case, however, *cubic* diamonds would have to show the [0001] axis associated with the

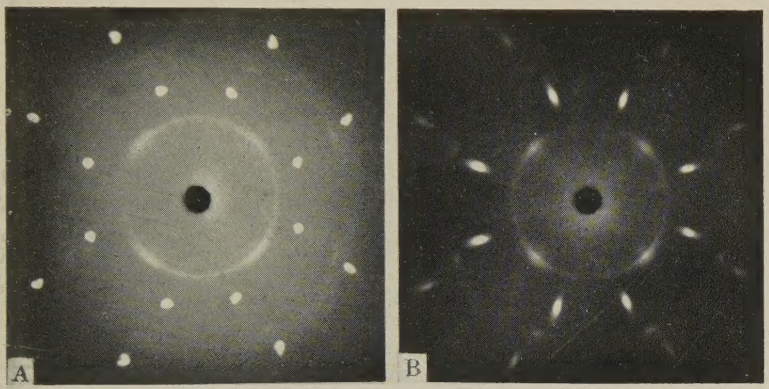


FIG. 2. Laue photographs (×0·8) of diamond: A, octahedral crystal; B, cubic crystal.

[001] vertical, X-ray beam along [100], crystal 2·5 cm. from film. Filtered copper radiation, 30 kV, 15 mA, ½ hour.

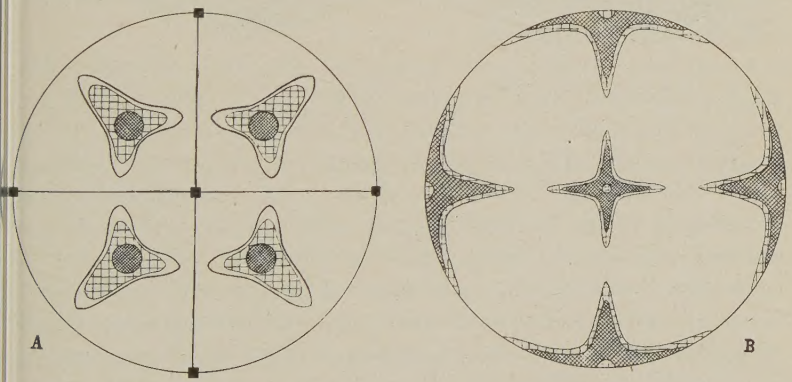


FIG. 3. Pole figures showing the preferred orientation of graphite (0002) in: A, Diamond graphitized by heating. B, Cliftonite from the Youndegin meteorite.

cube axes. Accordingly, some natural cubes of Belgian Congo diamond of edge approx. 1 mm. (the smallest which could be obtained) were kindly made available for this work by A. Triefus & Co., to whom I am grateful for this courtesy. It was while preliminary photographs of these specimens were being obtained prior to heat-treatment in order to

establish the presence or absence of anomalous reflections[1] that the spontaneous divergent-beam pattern was discovered.[2]

(ii) *Cliftonite.* Sir Lazarus Fletcher[3] isolated (1887) from the Youndegin meteorite about 100 crystals, averaging 0·2 mm. edge, which were of cubic habit and had the chemical properties of graphite. He made a careful morphological examination of these crystals and endeavoured (1899) unsuccessfully to find more of them. Further specimens have,

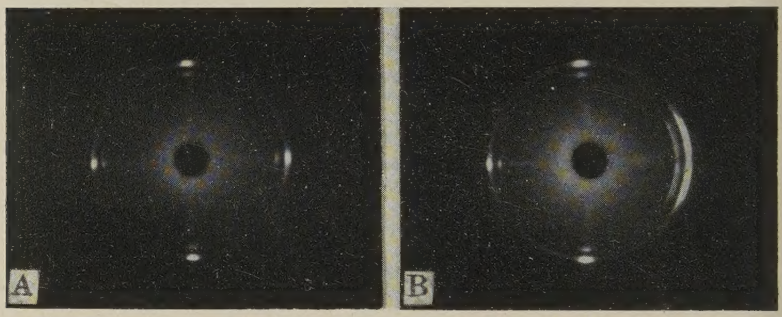


FIG. 5. Laue photographs (same size) of cliftonite from the Youndegin meteorite. Specimens 2·5 cm. from film, [001] vertical. 30 kV, 15 mA, ½ hour. A, filtered copper radiation, X-ray beam along [100]. B, unfiltered copper radiation, X-ray beam at 10° to [100].

however, been located in other meteorites. The X-ray rotation photograph published by Hey (loc. cit.) in which one of these crystals was mounted with a cube edge vertical, showed that the crystal was indeed graphite, and that there was some indication of preferred orientation of the [0001] axis along the cube axes of the crystal (a similar photograph is shown in fig. 4A, pl. XXVI, and a powder photograph of natural graphite is shown in fig. 4B, pl. XXVI for comparison). This was not the orientation that would have been expected for diamond, and so several crystals of cliftonite were kindly lent to me by the Mineral Department of the British Museum in order to confirm or extend this X-ray analysis. Hey's result was confirmed for all ten crystals examined, and indeed on Laue photographs the preferred orientation was found to be even sharper than he had thought (fig. 5A). A specimen of good cubic form was set visually with a [100] axis vertical, and a systematic preferred orientation determination was made. The resulting pole figure is shown in fig. 3B.

[1] K. Lonsdale, Proc. Roy. Soc. London, Ser. A, 1942, vol. 179, p. 315. [M.A. 8–284.]

[2] H. J. Grenville-Wells, Nature, London, 1951, vol. 168, p. 291.

[3] L. Fletcher, Min. Mag., 1887, vol. 7, p. 121; 1899, vol. 12, p. 171.

The difference between this and the corresponding diagram for graphitized diamond (fig. 3A), even of cubic habit, is striking. In fact, unless the preferred orientation found for diamond is strongly dependent on the conditions of graphitization, and these are very different in the meteorite from anything obtainable in the laboratory (as well they might be), there does not seem to be the slightest possibility that cliftonite is a pseudomorph after diamond. A definite conclusion on this point cannot,

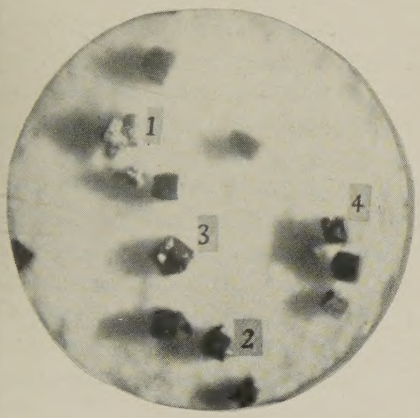


FIG. 6. Cliftonite from the Youndegin meteorite, Western Australia. ×20.

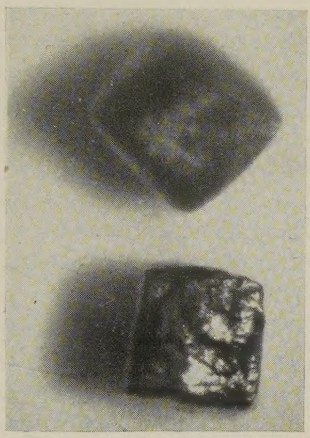


FIG. 7. Graphitized diamond cubes. ×20.

however, be reached until suitable natural graphite-coated diamonds have been examined.

The morphology of the cliftonite is also rather peculiar. Several crystals are shown in fig. 6, and the two graphitized diamond cubes are shown in fig. 7 for comparison. Most of the features noted by Fletcher can be seen in fig. 6; firstly, many of the crystals carry globular or acicular projections (1, 2). An interpenetrating twin of two cubes (the fluorite type) can be seen at (3), and one crystal in which faces of the form $\{hk0\}$ appear to have developed can be seen as well (4). Fletcher also reported that some of the crystals were hollow, and all the X-ray photographs obtained in this work show the (0002) ring split, as can be seen in fig. 5B—particularly in the Cu-$K\beta$ powder ring. This could be reproduced artificially by mounting a small quantity of graphite powder in seccotine *round* the end of a glass fibre, so that the graphite was effectively in the form of a hollow tube; thus the hollowness of the crystals might

be a general phenomenon, as suggested by the low density of the cliftonite ($\sim 2{\cdot}12$ gm./c.c.) as compared with that of graphite, and this certainly provides the simplest explanation of the split (0002) reflection.

Another interesting peculiarity is the weakening of the preferred orientation in the region of about 2° in all directions about the ⟨100⟩ directions, as can be seen in fig. 5B; such an effect is known in other meteorite minerals which are regarded as pseudomorphs (information supplied by Dr. M. H. Hey).

The one point of similarity between the graphitized diamond and the cliftonite is that in both cases the (0002) reflection is very sharp, whereas the second ring is relatively diffuse, and there are no sharp rings at angles approaching $\theta = 90°$. The nature of the graphite itself does thus appear similar in the two cases.

No alternative explanation of the origin of cliftonite has been found. The possibility that anything of this type is to be found in nickel-iron alloys of composition similar to that in the meteorite is exceedingly remote (H. G. Morrough, private communication), so that it seems almost certain that it is a pseudomorph of some kind and not a spontaneous formation. It might be profitable to re-examine some meteoritic diamonds to see whether there is any incipient graphitization, and if possible to graphitize diamond at very high pressures.

(*b*) *Graphite-coated diamonds from Premier mine, South Africa.*—A. F. Williams[1] states that 'Graphite-coated diamonds are found in every mine, but are more common in some mines than others. Especially well-preserved specimens are of quite common occurrence in the Premier mine.' Williams goes on to describe a number of specimens in detail, but no information which enabled a decision to be reached on the method of formation was obtained, apart from the fact that the graphite showed great chemical refractoriness, which suggested that it has been formed at a very high temperature (Wagner, loc. cit.).

Two such specimens kindly lent to me by the British Museum were examined by X-rays. Unfortunately these were large crystals (about 6 mm. diameter) and thus rather unsuitable for X-ray work, but no others were available. One specimen (B.M. 1910,222, weight 0·368 gm.) is an octahedron. Laue photographs showed that this diamond, while mainly a monocrystal, is of very poor quality and showed some fragmentation. No trace of graphite could be detected on an exposure of

[1] A. F. Williams, The genesis of the diamond. London, 1932, vol. 2, p. 434.

hour at 15 mA. Similar results were found in cases of artificial graphitization (or attempted graphitization) as mentioned in section (*d*) below.

The other specimen (B.M. 1910,223, weight 0·430 gm.) of irregular shape though it has roughly the form of a cube modified by a form {*hk*0}, was set in what was assumed to be an orientation in which the X-ray beam would coincide with a fourfold axis. The resulting photograph is shown in fig. 8, and it is curious that with such complete absence of discrete Laue spots there is not a greater development of diamond powder rings. This indicates that the specimen was originally a monocrystal, and not a randomly oriented collection of crystallites like carbonado. As can be seen, there is again no trace of a graphite powder ring. The general appearance of some of the patches of small spots is, however, very similar to those obtained on photographs of gem diamond which has been graphitized (section (*d*) below), although in fig. 8, pl. XXVI, the process has obviously been carried very much farther. The failure to observe graphite on these specimens is disappointing, and it is hoped that some small crystals really suitable for X-ray examination will be obtainable.

(*c*) *The nature of the graphite formed.*—It can be seen that the graphite itself is of a somewhat unusual form. The strongest lines of the normal graphite powder pattern are visible and are indexed in table I.

TABLE I. Indexing of X-ray photograph of cliftonite (fig. 4A, pl. XXVI).

hkil	Sharpness (visual estimate).	θ_{hkil} (calc.)	θ_{hkil} (obs.)
0002	sharp (split)	13·30°	13·31°
$10\bar{1}0$	quite sharp	21·22	21·24
$10\bar{1}\frac{2}{3}$	quite sharp	21·72	21·81
$10\bar{1}1$	not defined	22·32	—
$10\bar{1}\frac{4}{3}$	not defined	23·16	—
0004	slightly diffuse	27·40	27·37
$11\bar{2}0$	very sharp	38·83	38·80
$11\bar{2}2$	rather diffuse	41·94	41·82
0006	rather diffuse	43·65	43·52
$20\bar{2}0$	very diffuse	46·43	—
$20\bar{2}\frac{2}{3}$	lines not resolved	46·76	~ 46·73
$20\bar{2}1$	—	47·18	—
$20\bar{2}\frac{4}{3}$	—	47·77	—
$11\bar{2}4$	very diffuse	53·37	~ 50·97

The Bragg angles were calculated using Lipson and Stokes' values of the lattice constants, i.e. *a* 2·456, *c* 6·696 Å., and the wave-length of Cu-$K\alpha$ radiation 1·541 Å. The measured values were obtained from fig. 4A, pl. XXVI. The excellent agreement obtained is to some extent fortuitous,

as no corrections have been applied. The 0006 reflection is probably visible only because of the strong preferred orientation which gives it enhanced intensity at the equator. No lines having higher θ-values can be detected.

The resolution obtainable with a 3 cm.-radius camera is not really sufficient to warrant a detailed analysis of the powder pattern, but by comparing the original negatives of the cliftonite and of natural graphite the most important difference can be seen to lie in the group of four closely spaced lines $10\bar{1}0$, $10\bar{1}\frac{2}{3}$, $10\bar{1}1$, and $10\bar{1}\frac{4}{3}$. In natural graphite, $10\bar{1}1$ is considerably stronger than the other three (as can be seen in fig. 4B), whereas in cliftonite $10\bar{1}0$ and $10\bar{1}\frac{2}{3}$ are clearly defined while $10\bar{1}1$ and $10\bar{1}\frac{4}{3}$ do not appear as discrete lines at all, although there is quite a strong broad diffuse ring in this region. (This detail does not reproduce clearly in the photographs.) As pointed out by Lipson and Stokes (loc. cit.) the sharpness of the $11\bar{2}0$ reflection indicates that the hexagonal layers themselves remain perfect.

The relative prominence of $10\bar{1}\frac{2}{3}$ might seem to be an indication that the proportion of β-graphite present is higher than usual, in accordance with Nath's hypothesis, but $10\bar{1}\frac{4}{3}$, which is also a β-graphite reflection, does not appear as a discrete line. An arrangement of layers which would account for the observed diffraction effects has not yet been worked out. This particular pattern does not approximate to any of the photographs published by Miss Franklin[1] for graphite of varying probabilities of disorientation between successive layers.

(*d*) *Effect of heat-treatment on the diamond itself.*—The formation of graphite could just be detected by means of X-rays on one blackened octahedron (treatment unspecified). This specimen showed no anomalous streaks, and a fairly strong spontaneous divergent beam pattern. No graphite could be detected on a Laue photograph of 1 hour's exposure at 15 mA for a large diamond which had been raised to 1820° C. in $2\frac{1}{2}$ minutes and then allowed to cool, although it was completely blackened.

(i) *Diamonds heated to 2000° C. in a carbon block.*—Three diamonds which had been raised to 2000° C. in two minutes were much blackened and broken, and fragments of these were tested. All gave strong graphite powder patterns, in which the 0002 ring in particular showed strong preferred orientation, in addition to the diamond pattern. A Laue photograph of one piece showed, instead of sharp Laue spots, collections of small spots which sometimes lay on short lines radiating from a centre and indicating that the breaking-up of the crystal had not been entirely

[1] R. E. Franklin, Acta Cryst., 1951, vol. 4, p. 253.

ndom. The fine structure of these Laue spot groups was not investiated.

A small fragment in the form of an octahedral plate gave a divergent-eam photograph (using an iron foil)[1] which showed very fine lines, and roduced very good sharp Laue spots, although irregular patches near ne strongest reflections showed that there had been some breaking-up f the crystal. In all these photographs it could be seen in a general way nat the preferred orientation of the graphite 0002 reflection was asso-ated with the diamond [111] axes.

Another fragment in the form of an octahedral plate showed quite rong anomalous reflections (Lonsdale, loc. cit.), and it could be seen om the Laue spots that again the main portion of the diamond had mained a good monocrystal. A complete series of photographs for the xamination of these extra reflections was taken with Cu radiation.

(ii) *Diamonds heated in a carbon arc.*—Through the kindness of Mr. . W. Anderson in providing the necessary facilities, experiments were nade on the possibility of graphitizing diamonds directly in a carbon arc. em octahedra were placed in a shallow recess in a carbon block and eld for periods of up to five minutes in a carbon arc, where they could e seen glowing almost as brightly as the arc itself, and must have eached a high temperature. They were completely blackened, but a pecimen which had previously shown strong extra streaks still did so, nd showed no traces of graphite on a photograph of moderate exposure; owever, an iron-foil divergent-beam photograph showed the develop-nent of an extremely fine sharp (111) conic, which is not usual for perfect iamonds, and may indicate that some breaking-up of the crystal ad occurred. One diamond octahedron which had become partially lackened did, however, show some X-ray evidence of graphite formation.

These experiments indicated that diamond could not be satisfactorily raphitized in a carbon arc, partly because the temperature reached ould neither be measured nor controlled, and partly because the heating ook place in the presence of oxygen, which favours the formation of CO r CO_2 rather than of graphite. These experiments were therefore not ursued farther.

(iii) *Diamonds heated in a vacuum furnace.* -A special vacuum furnace mall enough to be heated in an arc, and whose temperature could be ontrolled and measured, was designed for experiments of this kind by r. E. Billig, to whom I am greatly indebted for the time and trouble e has spent on the graphitization of diamonds for this investigation.

[1] H. J. Grenville-Wells, Thesis, London University, 1951.

Preliminary tests to determine suitable conditions of graphitizatio were made on five gem octahedra and two Congo cubes. It is the result on this batch which are discussed here, further experiments having bee unavoidably delayed. Diamonds sawn to provide (100) and (110) plane in addition to natural (111) faces will also be graphitized to test the rela tive ease of graphitization of different crystallographic surfaces.

As can be seen in fig. 2A the gem octahedron has retained its mono crystalline form and still gives sharp Laue spots. It gives a weak, sharp divergent-beam picture. The two cubes, on the other hand, have alterec very strikingly. Fig. 9, pl. XXVI, shows an iron-foil divergent-bean photograph of such a diamond before heat-treatment, and fig. 10, pl XXVI, shows one of the cubes after heating to 2000° C. (both cubes giv exactly the same type of photograph). Here the Laue spots are quit diffuse, and the divergent-beam conics are much less well-defined although outwardly the crystals do not appear to have altered, excep that they are blackened.

These cubes were quite opaque and strongly coloured before treat ment. It is therefore possible that they contained impurities which hav either altered or been driven off at the high temperature, and this ha caused the complete deterioration of the crystal. Further experiment with Congo diamonds would be of interest. Although Fe and Si wer found in two such cubes by spectrographic analysis (carried out by Mis Czapska of Hilger's Ltd., to whom I am much indebted for doing this) other Congo diamonds have been shown to contain different impurities and it would be unwise to generalize about the influence of impurities

As regards the original intention to see whether heat-treatment coul transform Type I diamond[1] into Type II, or vice versa, it certainl proved possible to increase the mosaicity of the diamonds, but the ex periments met with no success whatever in affecting the intensity of th anomalous streaks. The position in this respect may be summarized a follows:

Extra streaks were not observed to appear in any diamond from whic they had previously been absent: i.e. we could not turn a Type I (mosaic) diamond into a Type I (perfect) diamond by some kind c annealing process. This does not necessarily mean that this is impossibl because the heat-treatment used was a violent one of rapid heatin followed by immediate cooling, and was probably quite unsuitable fo such annealing.

[1] R. Robertson, J. J. Fox, and A. E. Martin, Phil. Trans. Roy. Soc. Londo Ser. A, 1934, vol. 232, p. 463. [M.A. 6–6, 494.]

Diamonds (whose previous quality was unknown from an X-ray standpoint) which had been heated to 2000° C. and showed appreciable graphite-formation and fragmentation, also showed quite strong extra effects, and sharp Laue spots indicating that the greater part of the specimen was still a good single diamond crystal. A complete set of Laue photographs indicated that the extra reflections were of the usual type, though satellite reflections resulting from fragmentation made it difficult to see them properly.

Gem diamonds which had originally shown strong extra streaks and which after graphitization showed the development of divergent beam effects, indicating that their texture had become increasingly mosaic, still showed undiminished extra streaks. This persistence is a strong indication that the anomalous streaks are not some kind of perfect-crystal effect, but represent some defect structure which is not appreciably affected by heating.

Acknowledgements.—In addition to the acknowledgements made in the text, I am indebted to Dr. W. Campbell Smith, Dr. F. A. Bannister, and Dr. M. H. Hey of the Mineral Department of the British Museum for their interest in this work and for helpful discussions. I should like to thank the Diamond Corporation for the provision of a collection of gem diamonds from which some of these specimens were taken; and Industrial Distributors (1946), Ltd., for financial assistance enabling me to undertake the research of which this work forms part. Finally, it is a pleasure to record my gratitude to my supervisor, Professor Kathleen Lonsdale, for much valued advice and encouragement during the course of this work.

Summary.—Diamond heated in vacuo to about 2000° C. is wholly or partially converted to graphite which has a strong preferred orientation, the [0001] axis of the graphite being associated with the diamond [111] axis irrespective of the original habit of the diamond. The preferred orientation of the graphite in cliftonite, however, has been shown to involve the association of the [0001] axis with the cube axes of the crystal, thus casting doubt on the possibility that cliftonite is a pseudomorph after diamond. The graphite itself appears in both cases to be imperfectly crystallized, and is neither α- nor β-graphite, nor the usual mixture of the two. It has been shown by means of divergent-beam X-ray photographs that the mosaicity of diamonds can be increased by heat-treatment.

Explanation of Plate XXVI.

X-ray photographs ($\times 0{\cdot}62$) of diamond, graphite, and cliftonite.

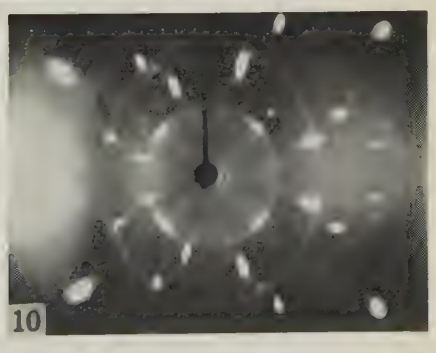
Fig. 4a. Cliftonite from the Youndegin meteorite, Western Australia. Rotation photograph with [001] vertical. Filtered copper radiation, 30 kV, 15 mA, 3 hours.

Fig. 4b. Natural graphite, Powder photograph. Filtered copper radiation, 30 kV 15 mA, $3\frac{1}{2}$ hours. Specimen rotated.

Fig. 8. Graphitized diamond from Premier mine, South Africa. Cylindrical Lau photograph, radius 3 cm., X-ray beam along [100]? Brass target, Cu-Zn radia tion, 45 kV, 10 mA, 2 hours.

Fig. 9. Diamond, cube from Belgian Congo. Cylindrical Laue photograph, radiu 3 cm. [001] vertical, X-ray beam along [100]. Copper radiation with iron foil 30 kV, 15 mA, 2 hours.

Fig. 10. Diamond, cube from Belgian Congo. After being heated to 2000° C Cylindrical Laue photograph, radius 3 cm. [001] vertical, X-ray beam almos along [100]. Copper radiation with iron foil, 30 kV, 15 mA, $1\frac{1}{4}$ hour.



H. J. GRENVILLE-WELLS: X-RAY PHOTOGRAPHS OF DIAMOND, GRAPHITE, AND CLIFTONITE

On the occurrence of varlamoffite (partially hydrated stannic oxide) in Cornwall.

By Sir Arthur Russell, Bart.

and E. A. Vincent,[1] B.Sc., Ph.D., A.R.I.C., F.G.S.
Lecturer in Mineralogy, Durham Colleges in the University of Durham.

[Read November 1, 1951.]

Characters and mode of occurrence (A.R.).

As long ago as 1906 I had noticed a yellowish clay-like mineral occurring somewhat abundantly at both Cligga mine, Perranzabuloe, and at Bunny mine, St. Austell. From its appearance the mineral did not look particularly interesting, neither did it suggest being one containing a metal, and for these reasons no attempt was made to determine its character. In a paper read before this Society in 1937 I mentioned this yellowish clay-like substance as occurring associated with rashleighite at the Bunny mine.[2] Soon after the publication of this paper in 1948 I received a letter from Monsieur N. Varlamoff in the Belgian Congo saying he had seen my reference to the 'yellowish clay-like substance' (p. 356) and suggested it might possibly be identical with the mineral varlamoffite which he had recently discovered in the Belgian Congo and which had been named after him, his description of the mineral with analysis, mode of occurrence, and localities having been published in 1948.[3] Sure enough, on examination I found both the Cligga and Bunny minerals to contain a high proportion of tin. Through the interest of Professor K. C. Dunham, Dr. E. A. Vincent of Durham University most readily and kindly undertook the full chemical examination of this somewhat remarkable and puzzling material—a quite tricky

[1] Now University Demonstrator in the Department of Geology and Mineralogy, University Museum, Oxford.

[2] A. Russell, On rashleighite, a new mineral from Cornwall, intermediate between turquoise and chalcosiderite. Min. Mag., 1948, vol. 28, pp. 353-358.

[3] N. Varlamoff, Matériaux pour l'étude du minéral jaune d'étain (varlamoffite): occurrence, géologie et origine du minéral. Ann. (Bull.) Soc. Géol. Belgique, 1948, vol. 72, pp. B41–B46. [M.A. 10–454.]

task. In the following notes I have attempted to describe its characte and mode of occurrence.

Cligga mine (formerly a part of Perran Great St. George mine) Perran zabuloe, Cornwall. (Six-inch Ordnance map, Cornwall, 48 NW., 1908.)— The small granite mass traversed by countless small mineral veins wit greisen walls which forms the 300-feet high Cligga Head has been worke for tin from time immemorial, and latterly for both tin and wolfran The cliff itself is honeycombed by old workings, the visible numbers c which are continually altering in appearance owing to the frequent fal of cliff. The area occupied by the top of the cliff is covered with graniti and greisenized vein-stuff derived from the old workings, and it is hei that specimens of varlamoffite may still be found. The largest and be specimens which I have obtained were found during the carting away one of these old dumps near the cliff top in February 1939, and at th same time, while the mine was still at work, I found the mineral in sit in some of the small veins underground between the surface and th 300-feet level at the base of the cliff; here also a small vein of stannite still visible in the roof of one of the old levels. During the late workin of the mine there is every reason to believe that considerable quantiti of stannite and varlamoffite actually went through the mill, though course the only tin recovered was in the form of cassiterite.

The Cligga mine varlamoffite is a rather soft, somewhat clay-like co loidal mineral, in colour straw-yellow to massicot-yellow to cream-bu (colours of R. Ridgway). Under the microscope the surface of the pure material often shows a waxy glistening lustre resembling that of certa melts; here and there are blebs of colourless quartz of varying siz minute scales of mica, and occasionally small prisms of black tourm line. In some specimens the mineral forms layers up to an inch in thic ness, with quartz, on greisen; in others it occurs as very considerab masses with quartz and is permeated by long blades of wolfram and is associated with stannite, cassiterite, arsenopyrite, greyish-gre scorodite, and scales of white gilbertite.

The following is a list of the minerals which I have observed in t greisen veins of Cligga mine. Molybdenite rarely, cassiterite often w crystallized, stannite abundant, varlamoffite, wolframite abundant; a occasionally well crystallized arsenopyrite, scorodite, pharmacosideri native copper, chalcopyrite, olivenite, torbernite, topaz well cryst lized, lithia-mica crystallized as large plates, gilbertite, andalus rarely unaltered and pink in the contact-altered slate (killas).

Bunny mine, St. Austell, Cornwall. (Six-inch Ordnance map, Cornw.

41 SE., 1908). The Bunny mine varlamoffite differs from that of Cligga mine in being for the most part of an ivory-yellow colour and very occasionally primrose-yellow. It occurs, intimately associated with light blue-green rashleighite and blue turquoise, in layers up to 1½ inches thick in cassiterite and wolframite lodes with greisen walls traversing kaolinized granite, a description of which was given in my paper on rashleighite. The mineral also occurs alone filling crevices in bands of slightly smoky crystalline quartz. Both the varlamoffite and rashleighite occasionally contain small grains of fresh cassiterite and wolframite, associated minerals being stannite rarely, pyrite, arsenopyrite, chalcosine, fluorite, gilbertite, and tourmaline. The Bunny mine specimens of varlamoffite were obtained by digging into the engine shaft dump, and from a vein outcrop a little south of the southernmost of the two old pits.

Kit Hill Great Consols mine, Stokeclimsland, Cornwall. (Six-inch Ordnance map, Cornwall, 29 NE., 1907.)—The numerous cassiterite and wolframite veins with greisen walls which traverse the granite of Kit Hill seemed a likely locality for varlamoffite and I was rewarded by finding it here in May of this year (1951). The specimens were obtained from one of the many small dumps in an old open-cut on an east and west lode, north-east of the summit.

The varlamoffite is cream-buff to brownish-yellow in colour and exhibits a much more coarse colloidal structure than that from Cligga and Bunny mines. It forms layers up to ⅝ of an inch thick on quartz enclosed by greisen walls, and here again on two of the specimens a very small patch of unaltered stannite is visible in the quartz underlying the varlamoffite. A little black cassiterite, arsenopyrite, scorodite, mica, and tourmaline are also present in the quartz directly adjacent to the varlamoffite.

It may not be out of place to record here the localities in Cornwall at which stannite has been found:

Botallack mine, St. Just (H. S. Boase, 1822).
St. Michael's Mount, Marazion (W. Phillips, 1819).
West Wheal Providence (Wheal Conqueror), St. Erth (A. Russell, 1949).
Dolcoath mine (New Roskear shaft), Camborne (E. H. Davison, 1927).
Carn Brea mine, Illogan (J. Garby, 1947).
South Crofty mine, Illogan (T. M. Hall, 1868).
East Pool mine and Wheal Agar, Illogan (J. H. Collins, 1871).
Wheal Scorrier (Scorrier Consols mine), St. Agnes (R. Jameson, 1816). Requires confirmation.
Wheal Rock (afterwards part of West Kitty mine), St. Agnes (R. E. Raspe, 1785).
Wheal Kine (afterwards part of Polberro mine), St. Agnes (Alfred Fox colln.).

Cligga mine (formerly a part of Perran Great St. George mine), Perranzabuloe (A. Russell, 1939).

Stenna Gwyn mine, St. Stephen in Brannel (W. Gregor, 1800).

Bunny mine, St. Austell (A. Russell, 1944).

Kit Hill Great Consols mine, Stokeclimsland (A. Russell, 1951).

Barrier mine, Gwennap; Wheal Primrose, St. Agnes; and Lanescot mine, Tywardreath, are all mistakenly given as localities for stannite by J. H. Collins, 1871.

Chemical and X-ray examination (E.A.V.).

A complete chemical analysis has been made of the material from the Cligga mine, and confirmatory qualitative tests made upon the material from the Bunny mine and a sample of varlamoffite from the Belgian Congo.

Table I. Chemical analyses of varlamoffite.

	I.		Ia.	II.		III.
SnO_2 ...	65·8	H_2SnO_3 ...	37·79	59·22	Sn ...	25·8
Fe_2O_3 ...	9·23	SnO_2 ...	31·50	25·55	SiO_2 ...	25·8
FeO ...	0·37	$FeAsO_4.2H_2O$	14·31	—	Fe ...	8·9
CuO ...	0·63	Cu_2FeSnS_4	1·51	—	H_2O ...	11·89
As_2O_5 ...	7·13	SiO_2 ...	1·07	1·68	SO_4, As, Sb also present;	
S ...	0·44	Al_2O_3 ...	2·14	2·22	17·2 % Sn sol. in HCl;	
$H_2O+105°$ ...	6·26	Fe_2O_3 ...	4·31	9·45	$SnO_2.xH_2O$ 21·85 %	
$H_2O-105°$ ...	4·53	FeO ...	0·11	—		
SiO_2 ...	1·07	CuO ...	0·08	—		
Al_2O_3 ...	2·14	MgO ...	0·66	—		
MgO ...	0·66	WO_3 ...	1·27	—		
CaO ...	nt. fd.	Bi_2O_3 ...	0·77	—		
WO_3 ...	1·27	$H_2O-105°$	4·53	2·12		
Bi_2O_3 ...	0·77		100·05	100·24		
TiO_2 ...	nt. fd.			SnO_2 78·45		
MnO ...	trace			Sp. gr. 2·52–3		
	100·30					
Less O for S*	0·17					
	100·13					
Sp. gr. ...	3·13					

I, Material from Cligga mine, Cornwall. Analyst, E. A. Vincent.

Ia, Analysis I partially and tentatively recalculated.

II. Varlamoffite, Belgian Congo, average of three analyses. (N. Varlamoff, 1948; S. Gastellier, 1950.)

III. 'Souxite' (varlamoffite), Potosí, Bolivia. (R. Herzenberg, 1946 [M.A. 10–8].)

* Assuming all S present in stannite, Cu_2FeSnS_4.

The methods used in the chemical analysis of the Cligga mine material were largely based upon those given by Kallmann.[1] Decomposition by

[1] S. Kallmann, Importance, composition, and analysis of Bolivian tin concentrates. Indust. Engin. Chem. (Anal. Edit.), 1943, vol. 15, no. 3, pp. 166–174.

means of the low-temperature sodium peroxide frit, as described by Rafter[1] proved effective for preparing a solution of the material for general analysis. The value given for SnO_2 in the analysis is an average of four determinations—two iodimetric and two gravimetric—made upon rather small amounts of material, and though the agreement between these determinations is fair, the writer does not feel justified in quoting the average to two places of decimals. Copper was determined colorimetrically, and bismuth both colorimetrically and gravimetrically as BiOCl, the figure quoted being again the mean of the two results, which were in good agreement.

A qualitative spectrographic examination of a small fragment of the material was kindly made by Dr. L. Lund, of the Department of Geology, University of Leeds. In addition to the elements tabulated above Dr. Lund finds a small trace of silver, but no evidence for antimony, zinc, molybdenum, or vanadium.

The result of the analysis shows that the material is obviously not a definite mineral species, but a complex mixture, in which stannic oxide is the principal ingredient. Qualitative tests indicate also that the arsenic is present in the original material as arsenate. Because of this, and in view of the fact that the material occurs in association with stannite, an attempt has been made (column I*a*) to recalculate part of the chemical analysis.

If all the sulphur is combined with copper, ferrous iron, and tin in the stannite molecule, it is seen that this would account for most of the copper and ferrous iron in the analysis. It seems reasonable, also, to suppose that the arsenate ion may be combined with some of the abundant ferric iron in some form of ferric arsenate. It has been conventionally calculated as scorodite, $FeAsO_4.2H_2O$, though there is no evidence that this mineral exists as such in the mixture. The residual 'combined' water (given off above 105° C.) has been calculated into metastannic acid, H_2SnO_3, and the remaining tin left as stannic oxide. The degree of hydration of the stannic oxide in these materials is clearly indefinite. It is possible that some of the water given off below 105° C. may be loosely associated with more of the stannic oxide, but, in the absence of any precise evidence on this point, it is deemed best to state the 'hygroscopic' water separately. Some water will doubtless also be associated with the ferric iron and alumina remaining in the analysis.

In columns II and III of the table, analyses of varlamoffite from the

[1] T. A. Rafter, Sodium peroxide decomposition of minerals in platinum vessels. Analyst, 1950, vol. 75, pp. 485–491.

Belgian Congo and from Bolivia are reproduced for comparison. These appear to be simpler substances than that from the Cligga mine. Attention may be drawn in passing to the similarity in the values for silica, alumina, and ferric iron in the Congo and Cligga mine analyses. A small amount of arsenic was detected by the writer, using the Gutzeit test, in a sample of the Congo material sent by N. Varlamoff to Sir Arthur Russell.

No quantitative determinations have been made upon the small amount of picked material available from the Bunny mine, St. Austell, Cornwall. Qualitative tests show the presence of a high proportion of tin, and the total absence of arsenic. These tests, together with the evidence of the X-ray powder photographs, indicate that this material also consists mainly of partially hydrated stannic oxide, and is likely to be more closely comparable with the varlamoffite from the Belgian Congo than with the material from the Cligga mine.

X-ray powder photographs.

X-ray powder photographs have been taken of the partially hydrated stannic oxide materials from the Cligga, Bunny, and Kit Hill mines, Cornwall, and, for purposes of comparison, of the type varlamoffite from the Belgian Congo, a specimen of Cornish cassiterite from the mineral collection in the Durham Colleges' Department of Geology, and of air-dried 'metastannic acid' (prepared by dissolving pure metallic tin in dilute nitric acid and digesting the solution on the hot-plate). These photographs, in the form of positive prints, are reproduced in fig. 1. All were taken under identical conditions in a camera 9 cm. diameter, using Cu-$K\alpha$ radiation.

It is of interest to compare the resolution and the sharp definition of the lines in the cassiterite pattern (no. 5) with the broadened and ill-defined lines of the remainder. These remaining five patterns appear to consist of the most prominent lines of the cassiterite pattern; there are, perhaps, a few minor differences in spacing, but the essential identity of all the patterns is clear enough. No quantitative measurements have been made on the films.

The broadening of the prominent lines in the varlamoffite patterns, and the failure of the finer ones to be resolved at all, is presumably to be ascribed to the partly colloidal nature of these ochreous materials, which might be interpreted as mixtures of cassiterite and hydrated stannic oxide, with other impurities, in a very fine state of subdivision. In particular, the 'metastannic acid' prepared in the laboratory has given very

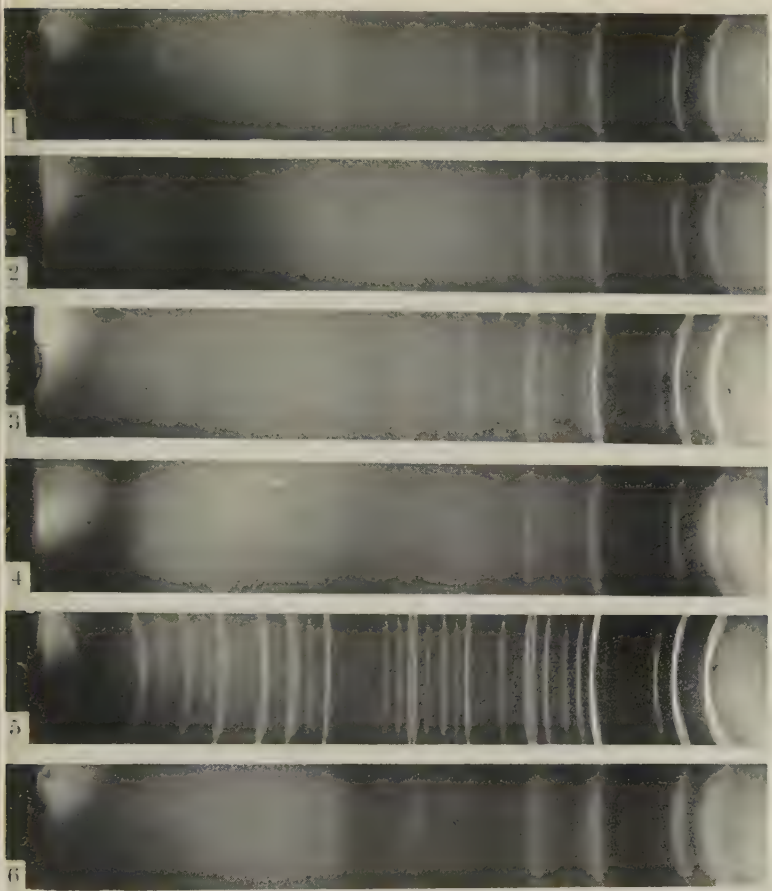


FIG. 1. X-ray powder photographs of stannic oxide materials. 1. Varlamoffite, Kalima, Maniema, Belgian Congo. 2. Arsenic-bearing varlamoffite, Cligga mine, Cornwall. (Analysis in table I.) 3. Varlamoffite, Bunny mine, Cornwall. 4. Varlamoffite, Kit Hill mine, Cornwall. 5. Cassiterite, Redmoor, Cornwall. 6. Hydrated stannic oxide ('metastannic acid') prepared in the laboratory.

broad and diffuse bands. It is stated in Dana's 'System of mineralogy' (7th Edition, 1944, p. 579) that 'Gels or sols of hydrous stannic oxide are formed by precipitating stannic salts with alkalies, and in other ways, and on aging give the X-ray diffraction pattern of cassiterite'.

Of the other patterns, that of the Bunny mine material is perhaps rather better defined than those of the Congo or the Cligga mine materials.

As far as can be made out, the pattern of the analysed material from

the Cligga mine shows no lines which are not part of the cassiterite pattern. It is scarcely to be expected that the minor ingredients would have any effect upon the X-ray powder pattern, but some manifestation of the presence of ferric arsenate might have been anticipated. This substance, if present, does not therefore occur as the well-crystallized mineral scorodite, but in a colloidal form which seems to have no effect other than to cause a more or less uniform scattering of the X-rays.

Conclusions.

Some degree of hydration of stannic oxide, then, does not cause a rearrangement of the cassiterite crystal structure, and it seems probable that the 'combined' water in these materials is held by a tenacious surface adsorption on to particles of stannic oxide of almost colloidal dimensions consisting of aggregates of relatively small numbers of cassiterite unit cells. It would appear to be difficult on theoretical grounds to accommodate water molecules into the rather compact body-centred tetragonal lattice of cassiterite without causing considerable disruption.

No study has been undertaken to determine the precise nature of the hydration, or to determine which of the various possible hydrated stannic oxides are in fact present.

In this connexion, it may be as well to state briefly Varlamoff's observations and conclusions concerning the origin of the varlamoffite in the Belgian Congo. Here, he writes (loc. cit., 1948, p. в 45), it is often found filling geodes lined with cassiterite, and moulded upon this mineral. These cassiterite crystals retain perfectly smooth and polished faces, proving that the earthy yellowish varlamoffite does not originate from alteration of cassiterite. Further, he records that stannite is traversed by veinlets of the yellowish material, which has obviously been formed at the expense of the stannite, replacing it along cracks. Similar yellowish material has also been found to replace other sulphides, such as chalcopyrite.

Finally, in the Belgian Congo occurrences, tetrahedral zonary growths of varlamoffite are found, which are regarded as pseudomorphs after stannite.

Since varlamoffite in the Cornish occurrences is associated again with stannite and wolframite in greisen veins, while scorodite and arsenopyrite are also present locally, it seems likely that a similar origin can be envisaged for the material in the Cligga, Bunny, and Kit Hill mines. A process of oxidation and hydration of stannite, perhaps with arseno-

pyrite or scorodite, seems far more probable than any direct hydration of such a stable mineral as cassiterite. Tiny specks of a sulphide mineral, identified as stannite, have been noted by Sir Arthur Russell in the Kit Hill material, and he also records scorodite.

Addendum.

Since the above paper was written, Dr. C. F. Davidson, of H.M. Geological Survey, has kindly drawn the authors' attention to two further papers, published in 1950, concerning the varlamoffite from the Belgian Congo.

In the first, H. Buttgenbach[1] discusses the naming of these hydrated stannic oxide materials, concluding that, although there is some doubt as to whether the Bolivian 'souxite' of R. Herzenberg[2] or the Congo 'varlamoffite'[3] of the late R. De Dycker has priority, the available descriptions of the latter are so much more complete and authentic that the name varlamoffite should be retained. He remarks also that X-ray patterns obtained from the Congo varlamoffite were identical with those of synthetic metastannic acid. (The X-ray photographs are not illustrated.)

The second paper, by S. Gastellier,[4] gives an account of the chemical composition and properties of the Congo material. This investigation is more complete than that which we have attempted on the Cornish examples, and evidence is given which seems to indicate the presence of actual metastannic acid, H_2SnO_3, in the mixtures. It is further suggested that some of the ferric iron may exist in some sort of combination with stannic oxide.

It is apparent that our work with these Cornish varlamoffites has led to much the same results as were obtained by the workers on the Belgian Congo material. Clearly, the X-ray photographs of the Cornish material, which are discussed above, must be similar to those obtained by Prof. E. Niggli and M. Lambot, and mentioned by Buttgenbach.

Arsenic, bismuth, tungsten, and other elements were sought in the Congo material, but not found. The presence of considerable arsenic in

[1] H. Buttgenbach, Souxite et varlamoffite. Bulletin des Séances, Inst. Roy. Colonial Belge, 1950, vol. 21, no. 2, pp. 409–411. [M.A. **11**–416.]

[2] R. Herzenberg, Nuevos minerales de Bolivia. Boletín Técnico, Fac. Nac. Ingeniería, Univ. Técnica, Oruro, 1946, no. 1, reprint 11 pp. [M.A. **10**–8.]

[3] H. Buttgenbach, Les minéraux de Belgique et du Congo Belge. Liège and Paris, 1947, p. 182. [M.A. **10**–354.]

[4] S. Gastellier, Note sur un minéral jaune trouvé par M. Varlamoff. Bulletin des Séances, Inst. Roy. Colonial Belge, 1950, vol. 21, no. 2, pp. 412–419. [M.A. **11**–416.]

our analysed material remains of interest. Even if some or all of this element were combined with ferric iron, as suggested above, the possibility that some of the iron might also be combined with stannic oxide in some way would not be ruled out.

The fact that all these materials so far analysed contain comparable amounts of ferric oxide may have some significance, and the authors agree with S. Gastellier that further researches would be desirable in order to try to confirm the existence of natural metastannic acid, either in the free state or in combination.

Acknowledgements. In conclusion, the authors wish to record their gratitude to Monsieur N. Varlamoff (evidently a very attentive reader of this Magazine) for sending a specimen of the Belgian Congo varlamoffite; to Dr. Lars Lund, of the University of Leeds, for making the spectrographic examination of the material from the Cligga mine; to Dr. C. F. Davidson for drawing their attention to the latest accounts of the Belgian work on varlamoffite; and to Professor K. C. Dunham for his interest and encouragement in the work.

The ledmorite dike of Achmelvich, near Lochinver, Sutherland.

By P. A. Sabine, Ph.D., A.R.C.S., F.G.S.[1]

Geological Survey and Museum, London.[2]

[Read November 1, 1951.]

In the Geological Survey memoir[3] a dike is recorded cutting the Lewisian gneiss near Achmelvich, north-west of Lochinver, Sutherland. At the time the mapping was carried out no thin section was prepared of the rock, and the dike was presumed to be a continuation of the Canisp porphyry dike which is exposed in the river Inver near Lochinver and farther south-east.

During an investigation of the post-Cambrian sills and dikes of Assynt and the adjoining districts of north-west Scotland, the writer examined the Achmelvich dike in some detail and recognized its affinities with the nepheline-syenites. It is the purpose of the present note to describe the field occurrence and petrography of the dike.

Field relationships.

The dike strikes west-north-west across the promontory at the mouth of Loch Roe (fig. 1) and cuts Lewisian gneiss, the foliation planes of which strike north-east and dip at steep angles to the south-east. The course of the nearly vertical intrusion is rather irregular. The best exposures are at its western end where it is about 3 feet thick. The edges are chilled against the gneiss and a banded structure is present near to the margin. Inclusions of gneiss in the marginal zone of the dike appear to have been derived from the contiguous gneiss. They have sharp edges and show no sign of reaction with the igneous rock. Spheroidal weathering of the dike occurs but is not prominent. Inland the dike decreases in width and is eventually lost beneath peaty ground.

[1] The work forms part of a thesis approved for the degree of Ph.D. in the University of London.

[2] Communicated with the permission of the Director.

[3] B. N. Peach et al. The geological structure of the north-west Highlands of Scotland. Mem. Geol. Surv. Great Britain, 1907.

At its eastern end on the shore of Loch Roe the dike is about $2\frac{1}{2}$ feet thick. It is nearly vertical, chilled at the contacts, and shows slight marginal banding. Inland its width decreases to less than a foot and the dike cannot be traced across the peaty ground of Fairait Mhòr.

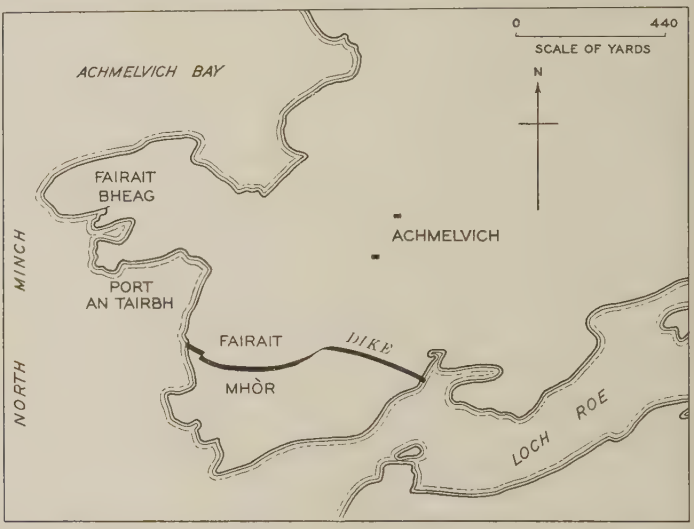


Fig. 1. Map of the area around Achmelvich, Sutherland. The position of the ledmorite dike is shown in black.

Petrography.

The freshest rock (Geological Survey slice no. S. 38132) is very fine grained and of mottled reddish- and greenish-brown appearance in hand-specimen. Under the microscope it is seen to be composed of a hypidiomorphic aggregate of alkali-felspar tablets in which there are distributed abundant needles of aegirine and numerous small dodecahedra of melanite. The felspar contains abundant needles of natrolite.

The aegirine needles, which are mainly fresh, reach 0·2 mm. in length. Melanite euhedra, up to 0·1 mm. across, are of deep brown colour and are sometimes rimmed by paler yellow garnet. Rarely the centres of the garnet crystals have altered to a colourless microcrystalline mineral of very low birefringence. The paler yellow garnet forming the rims of the original crystals is unaffected by this alteration, which has also been observed by the writer to be commonly developed in the similar ledmorites of Rhu More, Coigach.

Due to the presence of alteration products, determination of the felsic

nstituents of the rock is difficult. Orthoclase, the identity of which was nfirmed in the rock powder by its refractive indices $\alpha < 1{\cdot}519$, β 1·525, curs as tablets up to 1 mm. across. Natrolite is abundant in the felar, forming diverging bundles of needles. Its identity was checked by -ray powder methods after crushing the rock and separating the light action in bromoform. The resulting film showed only natrolite and lspar. Acid plagioclase was suspected in the thin section, but, due to e fine grain-size and many inclusions, could not be proved. In the rock wder small crystals of a biaxial doubtfully positive mineral, perhaps ulandite, were found having α 1·483, γ 1·490, but the mineral could t be distinguished in the thin section.

The rock has been analysed, with the results shown in table I, column I. ie specific gravity is 2·58.

ABLE I. Chemical composition of the Achmelvich ledmorite and similar rocks.

		I.	A.	B.	C.			II.
SiO_2	...	50·82	47·8	45·06	48·19	or	...	36·14
Al_2O_3	...	18·84	20·1	20·95	18·52	ab	...	17·03
Fe_2O_3	...	4·18	6·7	6·23	4·51	an	...	8·90
FeO	...	1·80	0·8	2·84	1·68	ne	...	13·78
MgO	...	0·92	1·1	3·31	1·12	no	...	2·13
CaO	...	5·47	5·4	8·32	10·29	il	...	1·67
Na_2O	...	5·62	5·5	3·51	3·44	pr	...	0·24
K_2O	...	6·14	7·1	4·09	8·05	mt	...	4·41
H_2O + 105° C.		4·42	2·4	3·98†	3·00	hm	...	1·12
H_2O − 105° C.		0·28	(ign.)	0·30‡	0·45	wo	...	4·99
TiO_2	...	0·88	0·7	1·25	1·75	di	...	4·97
MnO	...	0·38	0·5	—	trace	II. 6. (2) 3.3″		
BaO	...	—	0·8	—	—	Salemase		
P_2O_5	...	0·07	—	0·66	trace			
SO_2	...	nil	—	—	—			
	...	0·05	—	—	—			
CO_3	...	0·27	0·4	—	—			
	...	0·01*	—	—	—			
		100·15	99·3	100·50	101·00			
less O for S, Cl		0·03						
		100·12						

I. Ledmorite, Achmelvich. Analyst, W. H. Herdsman (new analysis). S. 38132.

A. Ledmorite ('borolanite'), Camas Eilean Ghlais, Rhu More, Coigach. Analyst, J. H. Player (Horne and Teall, 1892). S. 4390.

B. Ledmorite, Ledmore river. Analyst, A. Gemmell, Trans. Edinburgh Geol. Soc., 1910, vol. 9, p. 417.

C. Typical spotted borolanite, Am Meallan, Ross-shire. Analyst, W. Campbell Smith, Geol. Mag., 1909, dec. 5, vol. 6, p. 154.

II. Norm of analysis I.

* Determined by Mr. K. L. H. Murray in the Chemical Laboratory of the Geological Survey. † +110° C. ‡ −110° C.

Nomenclature.

The name borolanite[1] was proposed by Horne and Teall[2] in 1892 fo the group of rocks exposed in the Loch Borrolan mass, Sutherland 'especially characterised by the association of orthoclase and melanite They commented that 'The typical rock is a crystalline granular aggre gate of orthoclase and melanite. Biotite, pyroxene, alteration product after nepheline and sodalite, sphene, and apatite occur as subordinat and variable constituents.' One of the most striking features of the roc was stated to be the pseudo-porphyritic aspect due to the white or mor rarely pink patches, possibly representing original leucite.

'The affinities of borolanite are unmistakable,' wrote Horne and Teal 'It is a member of the foyaite (elæolite-syenite) family. The occurrenc of melanite as an important accessory in certain rocks belonging to th nepheline-leucite group has long been recognized. In our rock we hav melanite raised to the rank of an essential constituent.'

In an appendix to their paper they also described as borolanite th rock from the dikes of Rhu More, and noted that this was the only roc in which they had found typical aegirine. The Loch Borrolan mass an the dikes of Achmelvich and Rhu More are shown in fig. 2.

Professor S. J. Shand[3] restricted the use of the name 'borolanite' b designating melanite-syenite and melanite-syenoid rocks which contai less than 10 % by volume of melanite, whilst 'rocks containing ægirite augite in addition to (and replacing) melanite, and which lack the spotte or porphyritic character', he termed 'ledmorite'. This group he cor sidered might be regarded as a sub-group of borolanite. He referred t the Coigach rock as an 'unspotted borolanite', although he estimated i to contain 9·2 % by volume of melanite. He noted that certain 'point of difference must not be forgotten when that name (borolanite) is applie to it', and that the rock stands to the typical borolanites in much th same relation that ledmorite occupies.

The definition given by Horne and Teall appears to the writer, as did to Professor Shand, to require some limitation. It is therefore sug gested that the name 'borolanite' be applied to rocks consisting esse

[1] Borolanite was named after Loch Borolan, as it was then spelt. Followin customary Geological Survey practice place-names are here given as on the one-inc map, and the loch is therefore now spelt Borrolan.

[2] J. Horne and J. J. H. Teall. On borolanite—an igneous rock intrusive in th Cambrian limestone of Assynt, Sutherlandshire, and the Torridon sandstone Ross-shire. Trans. Roy. Soc. Edinburgh, 1892, vol. 37, pp. 163-178.

[3] S. J. Shand. On borolanite and its associates in Assynt. (Second communica tion.) Trans. Edinburgh Geol. Soc., 1910, vol. 9, pp. 376–416.

ally of orthoclase and melanite together with biotite, pyroxene, phelne or sodalite or alteration products of these minerals, sphene and patite, and characterized especially by the presence of white spots or tches fully or incipiently developed. Broadly, this is the definition wen by Shand. For other rocks which have close affinities with the rolanite type, but which lack the 'spotted' character, it is proposed

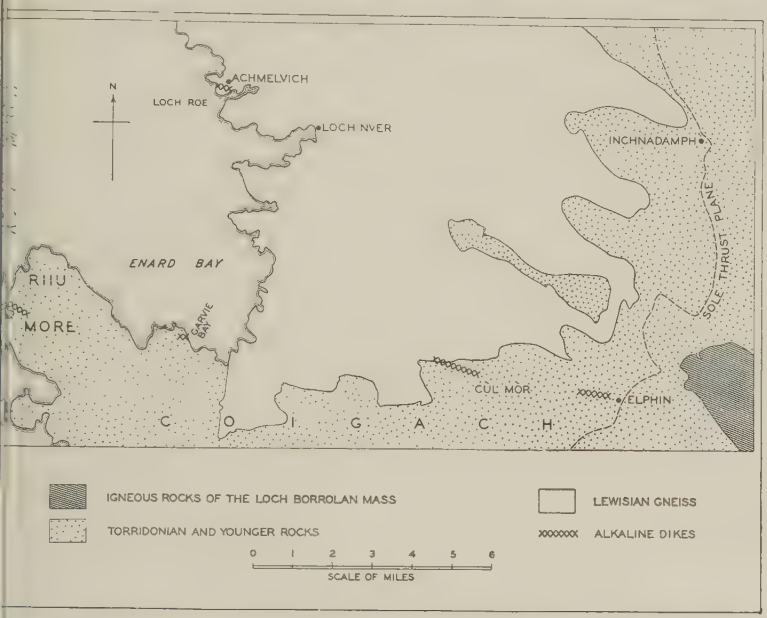


FIG. 2. Geological sketch-map of the district west and south of Inchnadamph, owing the post-Cambrian alkali-rich dikes.

at the name 'ledmorite' be used. Melanite and a felspathoid or its teration products are still essential constituents and either aegirine or girine-augite may also be present.

This nomenclature rather widens the use of 'ledmorite', but has the vantage of keeping 'borolanite' for the spotted rocks without requir- g another name for unspotted types—the natural history of which ay be fundamentally different—which did not hitherto fall into the ld covered by Shand's 'ledmorite'.

Professor A. Johannsen[1] records that in 1931 Shand (in litteris) with- ew the name ledmorite, but Johannsen recommended its retention for

[1] A. Johannsen. A descriptive petrography of the igneous rocks. Chicago, 1938, l. 4, p. 117.

the melanite-malignites, and the writer is therefore to a considerable extent following Johannsen. In his 1939 paper Shand[1] did not state clearly whether he proposed to withdraw or continue the use of the name. Since it fills a definite gap in petrographical nomenclature, the writer is of the opinion that it should be retained.

With the proposed usage, the rock of Achmelvich is to be classed as a ledmorite. The rock of Rhu More should also be referred to as ledmorite and not borolanite, a name which has hitherto given a false impression of the lithology to those who understand by 'borolanite' a nepheline melanite-syenite with large white spots which may have been leucite.

Age of the dike.

The dike is unfoliated and cuts the Lewisian gneiss but there is no other direct evidence of age. Closely similar, and in some cases almost indistinguishable rocks of post-Cambrian age outcrop farther south at Rhu More, Garvie Bay, Cùl Mòr, and Elphin (fig. 2), and there is little doubt that the Achmelvich dike belongs to the post-Cambrian pre-thrust movement period of igneous activity of Assynt.

Acknowledgements.—The cost of the chemical analysis was defrayed from a Royal Society grant which is gratefully acknowledged. The writer's thanks are due to Mr. A. J. Boyd of Inverkirkaig for collecting the specimen used for analysis.

[1] S. J. Shand, Loch Borolan laccolith, northwest Scotland. Journ. Geol. Chicago 1939, vol. 47, pp. 408–420.

The 'superposition error' in the micrometric analysis of rocks.

By R. B. Elliott, B.Sc., Ph.D., F.G.S.

Department of Geology, University of Nottingham.

[Taken as read November 1, 1951.]

troduction.—It is a well-known method in the measurement of birefringence to utilize a crystal's 'bevelled edge', on which appears a sequence of polarization colours, from that colour representing small relative retardation where the edge is thin, to a higher colour corresponding to the full thickness of the mineral in the microsection. In dolerites these bevelled edges on augites are extremely common and are very apparent between crossed nicols. In ordinary light, however, the majority of them are undiscernible and a grain appears to have uniform thickness over its entire area. The reason for the non-appearance of the bevelled edge in ordinary light is straightforward: the augites have excellent relief, that of the adjacent felspars is low; relief is a surface phenomena and independent of thickness, so that a thin edge of augite overlying felspar has the relief of augite, and the felspar is unnoticed.

It follows that in the measurement of the width of a grain of a high relief mineral, e.g. augite, surrounded by a low relief mineral, e.g. felspar, along any traverse we measure the maximum diameter of the high relief mineral, that is, from the tip of the bevelled edge on one side to the tip of the bevelled edge on the other. This will produce an inaccuracy, for we ought to measure from the centre of the bevel on one side to the centre of the bevel on the other. As a result of this inaccuracy we constantly overestimate the proportion of the high-relief mineral at the expense of the low-relief mineral.

In a normal dolerite this error will not be great because the bevelled edge is narrow compared with the diameter of the grain; however, the error will be there. As the grain diameter diminishes the distance between the bevelled edges on either side of the augite grains also diminishes until that grain-size is reached when the bevelled edges are adjacent—the mineral is all bevelled edge and has no uniform thickness.

The Rosiwal method of analysis assumes that the thickness of all

grains is the same, equal to the thickness of the slide, for only in th way can the volumes (areas × thickness) be proportional to areas an hence to lengths on a measured traverse. As mentioned above th thickness is not always constant, the average thickness of a small grai may be only half that of the slide and an error in the estimation c volumes from measured lengths is inevitable.

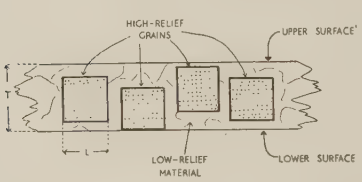


Fig. 1.

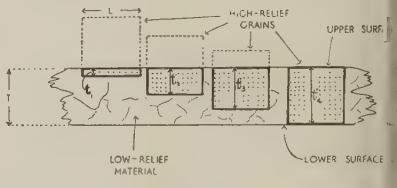


Fig. 3.

Fig. 1. Cross-section of a thin section assuming that all grains lie entirely withi the slide.

Fig. 3. Cross-section assuming that grains are cut by the upper and lower surfac of the slide.

This error is produced fundamentally because minerals of contraste relief overlap one another in the slide, and so it may conveniently b called the 'error of superposition'. With the aim of measuring this erro of superposition and its relation to grain-size the following calculation were made.

Calculations.—In order to make the subject amenable to computatio and as free as possible from mathematical intricacies, two assumption have been made regarding the shape and orientation of the grains. Thes are: (1) that the grains are cubes, and (2) that they are orientated so tha one face is parallel to the upper and lower margins of the thin sectio

(*a*) Let us assume that the cubic grains are all completely within th thin section and that none of them cut its lower and upper surfac (fig. 1).

In this case the assumed volume of the grain $= L^2T$ and the actu volume $= L^3$, where L is the length of one side of the cube and T is th thickness of the thin section.

$$\text{The \% error} = \frac{L^2T - L^3}{L^3} \times 100 = \frac{T-L}{L} \times 100.$$

When $L = T$, the error is zero; and as L decreases the error increase Fig. 2 shows the relation between % error and L, when $T = 0{\cdot}03$ mm

(*b*) The condition that all the grains fall within the thin section i never fulfilled, most of them will be cut by the surfaces of the thin sec

ion, so that the real volume will not be L^3 but L^2t, where t is the average thickness of cube within the thin section (average of t_1-t_4 in fig. 3).

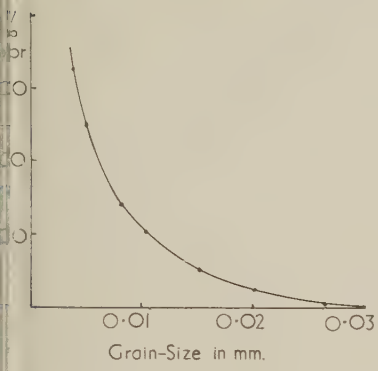


Fig. 2.

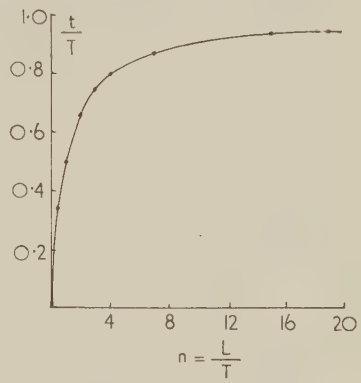


Fig. 4.

Fig. 2. Graph showing the relation between % error and grain-size on the assumption that all the grains are completely within the thin section.

Fig. 4. Graph showing the relation between t and L, both expressed as proportions of T.

This average thickness varies with the size of the cube. It is found that when $L = T, t = \frac{1}{2}T$; $L = 2T, t = \frac{2}{3}T$; $L = 3T, t = \frac{3}{4}T$; and generally

$$\text{when } L = nT, \qquad \text{then} \quad t = \frac{n}{n+1}T.$$

It can be seen that as the size of the grain, and n, increases, so t approaches T in value and the computed volume L^2T approaches the true value L^2t.

Fig. 4 shows the relationship between t and L, both expressed in terms of T, and illustrates how t/T approaches unity as L/T becomes large.

(*c*) Taking into consideration the relations:

$$L = nT \tag{i}$$

and

$$t = \frac{n}{n+1}T \tag{ii}$$

it is possible to relate grain-size and error.

The assumed volume of a grain $= L^2T$; the real volume $= L^2t$; the

$$\% \text{ error} = \frac{L^2T - L^2t}{L^2t} \times 100 = \frac{T-t}{t} \times 100.$$

Substituting $\frac{n}{n+1}T$ for t (ii),

$$\% \text{ error} = \frac{T - \frac{n}{n+1}T}{\frac{n}{n+1}T} \times 100 = \frac{100}{n}.$$

Substituting L/T for n from (i),

$$\% \text{ error} = \frac{100T}{L}; \qquad \text{(iii)}$$

$$\% \text{ error expressed in mm.} = \frac{3}{L} \text{ in slides of normal thickness.} \qquad \text{(iv)}$$

This error is plotted against L in fig. 5.

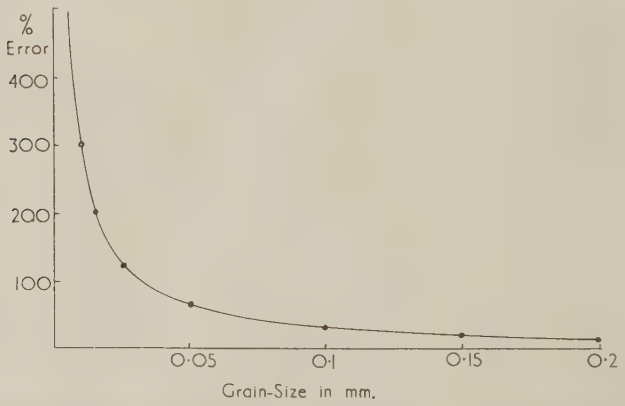


Fig. 5. Graph showing the relation between the % error and grain-size when the assumed volume is L^2t.

Conclusions.—1. The accuracy of the modal analyses of rocks with minerals of contrasted relief decreases rapidly with diminution of the size of the grains and in such a way that the superposition error in the estimation of the amount of high-relief mineral is a hyperbolic function of the grain-size.

The results show that for orientated cubes of constant size the error is 100 % for grains 0·03 mm. in diameter, 10 % for grains 0·3 mm. in diameter, and is not reduced to 1 % until the grains reach 3 mm. in diameter. Since the grains are not cubic and not orientated the exact

figures above have limited application, but the generalization of decreasing accuracy with decreasing grain-size remains independent of shape.

2. Where rocks are fine grained and have minerals of contrasted relief, modal analyses should be used for comparative purposes only and should not be used for the recasting of chemical composition.

3. Comparisons should be made with other rocks only when the rocks are of comparable grain-size. If not, some correction must be made.

4. The superposition error is proportional to T, the thickness of the microsection; it can therefore be reduced by carrying out modal analyses on sections thinner than normal.

5. The percentage of high-relief mineral present will influence the amount of the superposition error, for when it is very high small grains will pack underneath one another and increase t.

The thermal decomposition of afwillite.

By Mrs. K. M. Moody.[1]

Crystallographic Laboratory, Cavendish Laboratory, Cambridge.

[Read January 24, 1952.]

THE mineral afwillite is one of the hydrated calcium silicates which are found in set cements. It has the empirical formula $3CaO.2SiO_2.3H_2O$; a recent determination of the structure by Megaw (in press) has shown that the structural formula is $Ca_3(SiO_3OH)_2.2H_2O$, the hydroxyl groups being linked directly to silicon atoms. When afwillite is heated it loses water. Parry and Wright[2] observed that practically all the water could be driven off by heating for prolonged periods at 300° C., or for shorter periods at higher temperatures. They also found that a further reaction took place on heating to about 1300° C. The present work was undertaken to investigate these changes, and to identify the products formed, using X-ray powder methods.

Natural afwillite crystals from Kimberley, South Africa, were used. Samples of the mineral were crushed, placed in a small platinum boat, and heated in an electric furnace to temperatures 500–550° C., and to 1000° C. and 1300° C. The products were examined with a 9 cm. X-ray powder camera, using Cu-$K\alpha$ radiation. The substances present were identified by comparison of their powder patterns with standard photographs and with diffraction data recorded in the Amer. Soc. Testing Materials index. Where possible, identifications were confirmed by measurements of refractive indices.

The product obtained at 550° C. gave a very indistinct powder photograph, showing only a few diffuse lines at low angles, which indicated that the material was poorly crystallized. Nevertheless it was possible to identify the main constituent as γ-Ca_2SiO_4 (the low-temperature form with the olivine structure). The one observed line which could not be attributed to the γ-Ca_2SiO_4 pattern had the spacing $d = 3{\cdot}35$ Å. characteristic of quartz. Certain lines of the disilicate pattern were enhanced

[1] Now at Woolwich Polytechnic, London.

[2] J. Parry and F. E. Wright, Min. Mag., 1925, vol. 20, p. 277.

intensity relative to the others; they coincided in spacing (within the ther wide limits allowed by their diffuseness) with the strongest lines calcite, the presence of which was inferred. The dehydration reaction an therefore probably be represented by the equation:

$$Ca_3(SiO_3OH)_2.2H_2O \xrightarrow{550°C.} 3H_2O + Ca_2SiO_4 + SiO_2 + CaO, \quad (1)$$

e calcium oxide being converted to calcite by subsequent reaction with rbon dioxide, since no special precautions were taken to exclude this s from the furnace. No lines attributable to calcium oxide were tected in any photograph, but this does not rule out its occurrence in ry finely divided form.

Further evidence of the formation of calcite was obtained in a study the action of water on the dehydrated product. Samples of the hydrated material were left to stand in water contained in an open iver vessel, for times varying from a few minutes to several days. X-ray owder photographs showed the development of calcite, the calcite attern becoming stronger and sharper with increasing time of immer- on of the sample. It was concluded that the dehydrated product con- ined calcium oxide in amorphous form, which, in the presence of ater, reacted with carbon dioxide from the air to form calcite. No eaction other than the formation of calcite was detected in the rehydra- on experiments, and there was no reversion to afwillite or any of the her recorded calcium silicate hydrates.[1]

The products obtained by heating afwillite to 1000° C. and 1300° C. ave good powder photographs which were essentially alike. This attern was identified as that of rankinite, $Ca_3Si_2O_7$, by comparison with atterns obtained from the natural mineral from Scawt Hill, Co. Antrim,[2] nd from synthetic material of composition $3CaO.2SiO_2$. Spacings also greed with those given for rankinite in the Amer. Soc. Testing Materials dex. The final result of the reaction (neglecting possible intermediate eps) can therefore be represented by the equation:

$$Ca_3(SiO_3OH)_2.2H_2O \xrightarrow{1000°C.} Ca_3Si_2O_7 + 3H_2O. \quad (2)$$

The rankinite remained unchanged when allowed to stand with water. his was to be expected in view of the work of Flint, McMurdie, and Vells,[3] who failed to produce afwillite from the anhydrous silicate by

[1] H. F. W. Taylor, Journ. Chem. Soc. London, 1950, p. 3682. [M.A. 11–314.]
[2] C. E. Tilley, Min. Mag., 1942, vol. 26, p. 190.
[3] E. P. Flint, H. F. McMurdie, and L. S. Wells, Journ. Res. Nat. Bur. Standards .S.A., 1938, vol. 21, p. 628. [M.A. 7–283.]

hydrothermal methods, in contrast with its apparent ready production in nature (C. E. Tilley, loc. cit.).

A differential thermal analysis of afwillite was carried out by Dr. R. J. McLaughlin, of the Department of Mineralogy and Petrology, Cambridge. It shows an endothermic reaction proceeding in several steps in the temperature range 250°–450° C., the most marked reaction occurring at approximately 370° C.; and an exothermic reaction which takes place at about 820° C. It seems clear that these correspond to the dehydration process and to the formation of rankinite respectively.

The decomposition products of afwillite have thus been identified, but the mechanism of the reactions cannot be explained from present knowledge of the structures. Some interesting points may, however, be noted. If the intermediate reaction is correctly represented by equation (1), two-thirds of the calcium is converted to γ-Ca_2SiO_4 and the remaining third to CaO. It is not possible to explain how this change takes place, as the olivine-type structure of γ-Ca_2SiO_4 bears no obvious relation to that of afwillite, except in its possession of isolated SiO_4 groups. Megaw[1] has, however, found that in the structure of afwillite one calcium atom differs qualitatively from the other two in environment, and this fact may have some bearing on the decomposition. It is also interesting to note that Parry and Wright found a similar division of calcium, but this was in their high-temperature product. They record that after intense ignition two-thirds of the calcium became insoluble in dilute acid, while one-third remained soluble. In the present work, the high-temperature product has been identified as a single substance, rankinite, and it is difficult to reconcile this with Parry and Wright's result. Unfortunately it was not possible to repeat their solubility tests. A possible explanation might be that they were in fact working with the intermediate, not the high-temperature, product.

Preliminary work on the space-group and cell dimensions of rankinite has been carried out, and will be published elsewhere.

The co-operation of Dr. R. J. McLaughlin, who carried out the differential thermal analysis, is gratefully acknowledged. My thanks are also due to Professor Sir Lawrence Bragg and Dr. H. D. Megaw, for advice and encouragement during the course of the investigation, and to Newnham College for a studentship which made the work possible.

[1] H. D. Megaw, Acta Cryst., 1949, vol. 2, p. 419. [M.A. **11**–430.]